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UNITED STATES DEPARTMENT OF AGRICULTURE

In Cooperation with the University of Wisconsin and the Wisconsin Department of Agriculture

DEPARTMENT BULLETIN No. 1316

Washington, D. C. ▼ April 1925

SOME EFFECTS OF SODIUM ARSENITE WHEN USED TO KILL THE COMMON BARBERRY

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INTRODUCTION

For six years the United States Department of Agriculture, with the assistance of State and other agencies, has been waging a war on the common barberry in 13 of the North-Central States of the Union. Millions of bushes have been located, and their extermination has followed as rapidly as possible. The common barberry was not native in this area but had been extensively planted, and many escaped barberries had developed from seeds produced on the planted bushes and spread by birds and cattle.

Extermination of the plants by digging was soon found to be not only difficult but very expensive. This was especially true of those escaped bushes that had become established in stony ground or with their roots intertwined with those of large trees. When such bushes were dug, even small fragments of the roots left in the ground would usually sprout, necessitating not only a second or third visit to the place but often much additional work. An economical and effective method of killing these bushes therefore was sought, and many different chemicals were tried on small bushes, first in the

[1] The writers wish to acknowledge their indebtedness to Dr. W. E. Tottingham for suggestions and criticisms and to H. B. Parmele for assistance in analytical work.

greenhouse and later in the field if the greenhouse experiments seemed to warrant it. Among the most promising chemicals so studied was sodium-arsenite solution.

White arsenic, from which sodium arsenite is made, is produced in large quantities as a by-product from the smelting of ores of copper, silver, antimony, etc. Until recently the arsenic incidentally obtained by the smelting of ores for the metals was more than sufficient to supply the demand. However, with the spread of the cotton boll weevil in the Southern States and the growing use of calcium arsenate for the control of this pest the demand for arsenic has so increased that some ores are now being roasted primarily for the arsenic they contain. The principal sources of arsenic in the United States are Montana, Nevada, and Utah, though several other Western States, such as Colorado, South Dakota, Washington, and California, have deposits of arsenic-bearing ores (*29*)[2]. An idea of the production at some of the smelters may be gained from the figures of Haywood (*26*). He states that ores received at the smelter of the Anaconda Copper Co., in Montana, contain from 0.51 to 2.54 per cent of arsenic. As this smelter has a capacity of about 10,000 tons daily (*23*) it can be seen that large quantities of arsenic are produced, even though only from 25 to 50 per cent of it is recovered. A considerable quantity of white arsenic also is imported into the United States annually.

Since these studies were begun in 1921 the price of arsenic has about doubled, owing primarily to the greatly increased use of calcium arsenate for boll-weevil control. As has been shown by Heikes and Loughlin (*29*), the consumption of calcium arsenate in the United States, by years, during the five-year period from 1919 to 1923, inclusive, was as follows (pounds): 1919, 3,000,000; 1920, 6,000,000; 1921, 8,000,000; 1922, 16,000,000; 1923, 31,000,000. Even at its present price, arsenic should be considered when a weed eradicator is being sought.

HISTORICAL REVIEW

ARSENIC AS A WEED KILLER

Railroad companies in this country and elsewhere for a number of years have used large quantities of sodium arsenite to destroy weeds along their rights of way. Also many agricultural experiment stations have advocated sodium arsenite as a weed killer. In Vermont Jones (*34*, p. 185–186) used 1 pound of white arsenic to 2 pounds of washing soda diluted with 3 to 9 gallons of water and found that this solution destroyed all weeds except a few perennial grasses. Pure sodium arsenite proved quicker acting at a dilution of 1 pound in 4 to 8 gallons of water than did the preceding mixture. Stone (*41*) in Massachusetts found that dilutions of 1 part of sodium arsenite to 20 of water, 10 gallons to a square rod, killed plants, but new growth soon appeared. Large trees were not injured when the solution was applied 2 feet around their bases to kill poison ivy growing there.

Wilcox (*46*, *47*) reports that sodium arsenite in the form of a spray has come into general use in Hawaii to destroy weeds on rub-

[2] Serial numbers (*italic*) in parentheses refer to "Literature cited," at the end of this bulletin.

ber and sugar-cane plantations. One large sugar plantation alone has saved $100,000 on weeding through the introduction of the spray. Sal soda (2 pounds) and white arsenic (1 pound) were boiled together and subsequently diluted with 1 gallon of water, 100 gallons of this solution being used per acre. Killing effects were manifest two to three hours after spraying.

Gray (*13*, *14*) tried a sodium-arsenite spray on wild morning-glories in California. He made a stock solution of 10 pounds of caustic soda (98 per cent) and 10 pounds of white arsenic (99 per cent) with water to make 5 gallons. A gallon of this was used to 100 gallons of water, and 300 gallons were applied to the acre. From 85 to 90 per cent of the morning-glory roots were killed to the depth of 4 feet or more when the spray was applied to mature vines at the proper time (October). The second paper by Gray (1919) reports a failure of the spray for root killing at reasonable expense.

Hutcheson and Wolfe (*31*) in Virginia used one-half pound of sodium arsenite to 1 gallon of water for the control of hawkweed without injury to Kentucky bluegrass. The latter recovered much more quickly from the effects of arsenic than from salt. Burrows (*10*) found sodium arsenite useful in killing timber. He suggests the use of 1 pound of arsenic and 1 pound of washing soda or one-half pound of caustic soda to 4 gallons of water, and one-half pound of whiting for color. This he applied to the tree when dormant into frills cut entirely around the trunk.

TOXIC AND STIMULATING EFFECTS ON PLANTS

The extreme toxicity of arsenic to so many plants has indicated a possible danger from the too free use of sprays or weed killers which contain it, and considerable experimentation has been done to determine the effects of arsenic on the soil and on the germination of seeds and growth of plants. Greaves has investigated the influence of arsenic upon the biological transformation of nitrogen in soils (*15*, *16*), nitrogen-fixing power (*17*, *18*), and bacterial activities in the soil (*19*). He found that water-soluble arsenic may exist in soils to the extent of 82 parts per million without stopping ammonification and nitrification processes. Lower concentrations stimulated these processes and higher concentrations were toxic. Na_3AsO_4 became toxic at concentrations of 40 parts per million, and at 250 parts per million nitrification was stopped entirely. $PbAsO_4$ was not toxic at 400 parts per million. AsS_3 and $ZnAsO_4$ were only slightly toxic at the latter concentration. The greatest stimulation was noticed when the concentration of water-soluble arsenic in the soil was 10 parts per million. The bacterial activities of the soil were checked only with enormous quantities of arsenic. Small amounts stimulated soil bacteria and caused the liberation of insoluble plant-food materials, especially phosphorus.

Headden (*27*, *28*) found that orchard trees were sometimes killed by arsenic used in sprays. He demonstrated that orchard soil where arsenic sprays had been used contained as much as 138 parts of arsenic per million. The contention that insoluble arsenic as used in sprays was the cause of killing orchard trees was questioned by Ball (*3*, *4*). He stated that collar-rot and alkali were the principal

causes of death of orchard trees in the West, producing symptoms similar to those caused by arsenic. Grossenbacher (*21*) states that Headden's conclusions were unwarranted. However, work by Swingle and Morris (*43*) in Montana and later by Hotson (*30*) in Washington demonstrates that even the relatively insoluble arsenicals used in orchard sprays are capable of producing cankers which may develop into typical crown-rot in apple trees. They conclude that crown-rot is a condition which may be brought about by any one of a number of causes working together or separately and that arsenic poisoning undoubtedly plays a part in some of the cases.

From the work of Jadin and Astrug (*32*), who found small quantities of arsenic in 85 species of plants representing 30 families of flowering plants and mushrooms growing naturally and in healthy condition, it appears that Headden may have overemphasized the danger to plant growth from small amounts of arsenic in soil. Ampola and Tommasi (*1*) report that in nutrient solution it required 1 milligram of arsenic per liter of water to injure agricultural plants, whereas in soils growth was checked at concentrations corresponding to 0.3 milligram of arsenic per kilogram of soil. Voelcker (*45*) found that 0.02 per cent of soluble arsenic, such as sodium arsenite, when applied to soils in pot cultures caused crop failures; 0.05 per cent retarded germination of seeds; and 0.01 per cent, representing 825 pounds of arsenic acid per acre, had no ill effects on plants.

Gosio (*12*), working on the problem of accumulation of arsenic in plants, found arsenic noninjurious at low concentrations. He grew squash plants in boxes of soil and watered them with arsenical water, using a solution of 1 part of metallic arsenic to 1,000,000 parts of water, one month later changing to 1 to 100,000 and two months later increasing the concentration to 1 to 10,000 until maturity. The squash fruits contained 0.0041 per cent of arsenic and apparently were in good condition.

Brenchley (*9*) gives results of careful experimentation with arsenious acid added to soil in pot experiments. Adding the arsenic to the soil before seeding with barley, wheat, rye, and maize, 0.10 per cent of arsenious acid had no effect on the germination of barley, wheat, and rye, and maize withstood 0.40 per cent concentration without retarding germination. A concentration of 0.8 per cent was strongly adverse to germination of all plants tested. Growth was affected by 0.10 per cent concentration and in case of barley even by 0.05 per cent concentration. Rye proved more resistant than wheat. The results obtained by Wöber (*48*) agree with the above as to the order of susceptibility of plants. He studied the effects of smelter emanations containing arsenic on economic plants and placed them in the following order as to susceptibility: Legumes, barley, oats, wheat, maize, and rye.

The results obtained by Guthrie and Helms (*22*) on the limits of endurance of arsenic by certain plants run parallel to those of Wöber. In cultures in galvanized-iron pots the growth of barley was affected by 0.05 per cent concentration of arsenious acid, and growth was prevented by 0.10 per cent concentration. The germination of rye was affected by 0.20 per cent concentration, growth affected by 0.15 per cent, and growth prevented by 0.30 per cent.

In the recent work of Stewart and Smith (*38*, *39*) with pot cultures it was shown that arsenic in soil acts as a stimulant for certain plants. In the case of beans, potatoes, and peas 25 parts of arsenic per million of soil resulted in increased vigor. Wheat was stimulated with as high as 75 parts per million of soil and radish even with 250 parts per million. Most of the stimulated plants showed no increase in weight, but radish increased in size and weight. Susceptibility to arsenic varied with the different plants. Growth was checked by the following quantities (parts per million): Bean, 50; wheat, 52; potato, 78; pea, 193; radish, 940. When plants died from a killing concentration of arsenic the following quantities were found in the tissue (parts per million): Wheat, 269; potato, 524; bean, 678; radish, 940; pea, 1,190.

Stimulation by arsenic is reported also by Stoklasa (*40*) in the case of sugar beets. The arsenic was supplied through superphosphate in which there usually is 0.01 per cent of arsenic. Sugar cane was likewise stimulated. Jarvis (*33*) reported that copper arsenate bait, as used for white grubs, produced a noticeable stimulating effect. His controlled experiments in earthenware pots showed that treatments representing 113 and 226 pounds of Paris green per acre of sugar cane produced shoots averaging 10 inches as compared with 7.5 inches in the untreated pot. From 100 to 200 pounds of As_2O_3 (commercial) produced shoots of 27.8 inches as compared with 26 inches for the untreated.

TOXIC EFFECTS ON ANIMALS

The use of arsenic on the farm is always accompanied by more or less danger to the livestock. Farm animals, especially cattle, are attracted by the brackish sweet taste of arsenic solutions, according to Bevan (*6*). He reports that in 1908 many cattle were accidentally poisoned in the attempt to exterminate the locust (insect) with sodium arsenite. In dipping cattle, juice of the native aloe plant was added to the arsenic and acted as a repellent to keep the cattle from drinking the solution or licking each other. Barnum (*5*), of California, reported that where he used sodium arsenite for control of the morning-glory, stock had a preference for the sprayed plants. He also warns against the fumes which are generated where arsenic-treated weeds are burned. There evidently is a need for further investigation of substances which can be used with poisonous weed killers and which will act as repellents to livestock.

Since arsenic is attractive to animals, they may easily secure a fatal dose from treated plants or from poison bait or even from the ground where arsenic has been applied. Blyth (*7*) sets the standard medicinal dose of arsenic (As_2O_3) for adult humans at 2 to 5 milligrams; dangerous dose, 0.13 gram; for a horse the dangerous dose is 1.9 grams; for a cow 0.64 gram, and for a dog 32 to 64 milligrams. He says that poisoning of cattle can not occur through eating grass that has taken up arsenic from the soil through the roots. To quote (p. 535):

> It has, however, been shown by Gorup-Bezanez that if arsenious acid be mixed with earth and plants grown in such earth, they only take up infinitesimal quantities of arsenic. Hence, in cases of cattle poisoning, any defense based upon the alleged presence of arsenic in the pasture will be more ingenious than just.

Swain and Harkins (*42*) also think that plants do not absorb enough arsenic from the soil to poison animals. However, Formad's (*11*) investigations in the smelter region of the Northwest have shown arsenic deposited on pasture grasses to be a great menace to animals. He found arsenic in the grass and hay in amounts varying from 0.02 to 0.1 milligram of arsenious acid per gram of dry sample. Cattle, horses, and sheep feeding upon such grass and hay died by the thousands, evincing all the symptoms of arsenic poisoning as developed in experimental treatments, and there seemed no doubt that arsenic was the cause of death. Harkins and Swain (*24*) analyzed the animals fed on the grass and hay containing arsenic and found it in all parts of the animal tissues.

METHOD USED IN ARSENIC ANALYSIS

In the analyses for arsenic the generally accepted Marsh method and the modified Sanger-Black-Gutzeit method (*20*, p. 37) proved inadequate and time consuming as well as requiring an undue amount of attention. A combined modified method adapted from the methods of the Association of Official Agricultural Chemists (*2*, p. 56) and of Smith (*37*) was found effective and was therefore used for all the analyses reported in the following pages.

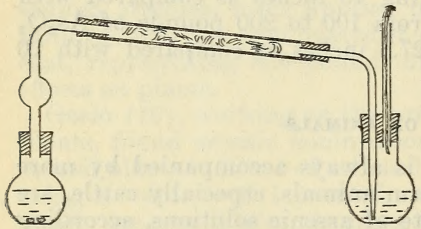


FIG. 1.—Apparatus used in arsenic determinations. Generating bottle on left and receiving bottle on right

DESCRIPTION OF APPARATUS

The apparatus was essentially of the type Smith has used (fig. 1) and consisted of a round 75-cubic-centimeter generating bottle connected through rubber stoppers by means of bent glass tubing to a horizontal heavy glass tube of 12 millimeters bore and 25 centimeters long, filled with absorbent cotton soaked in 5 per cent solution of $Pb(C_2H_3O_2)_2$ (to take up any H_2S produced in the generating bottle). The other end of the horizontal tube was similarly connected to a receiving bottle of 125 cubic centimeters capacity. In the extra hole of the rubber stopper of the receiving bottle was placed a glass tube with sensitized paper (strips of stiff white paper soaked for an hour in 5 per cent $HgBr_2$ in 95 per cent alcohol). The paper turns orange in contact with AsH_3 and serves as an indicator for the complete absorption of the gas.

PREPARATION OF SAMPLE

Two grams of finely ground barberry tissue were digested in a covered casserole over a low flame for 15 minutes with 5 cubic centimeters of concentrated HNO_3 and 20 cubic centimeters of concentrated H_2SO_4 (As-free). To the solution, while hot, were added at intervals small amounts of KNO_3 until all organic matter was destroyed and the solution appeared practically clear. After cooling, the solution was diluted with 50 cubic centimeters of water and boiled until all the nitric acid was expelled. This is necessary be-

cause AsH_3 can not be formed in the presence of oxidizing agents. The solution was then cooled and diluted to 200 cubic centimeters and filtered, if necessary.

PROCEDURE OF ANALYSIS

To 40 cubic centimeters of the above solution in the generating bottle, 4 cubic centimeters of 20 per cent solution of KI were added. This was then heated to 90° C., and four or five drops of $SnCl_2$ solution (40 grams $SnCl_2 2H_2O$ crystals made to 100 cubic centimeters with concentrated HCl) were added. The solution was kept at 90° for 10 minutes, then cooled, and pieces of As-free stick zinc, amounting to 5 to 8 grams, were dropped in and the bottle was connected to the apparatus. The KI and $SnCl_2$ were added to change the arsenic into the arsenious form; nascent hydrogen reduces arsenates with much more difficulty than arsenites. The $SnCl_2$ also takes up the liberated free iodine and, according to Parsons and Stewart (*36*) and Harkins (*25*), prevents the retention of arsenic by iron. According to these authors, retained arsenic was carried by hydrated iron oxide in solution when no $SnCl_2$ or salts of Bi, Cd, etc., were used. Fractions of a percentage of iron are found in the purest obtainable zinc.

Into the receiving bottle of the apparatus were poured 5 cubic centimeters of 5 per cent $HgCl_2$, and water was added to make the volume about 60 cubic centimeters. This solution was to receive and absorb the AsH_3 coming from the generating bottle. When arsine was passed in, the solution assumed a yellowish white tinge. Two hours were allowed for the reaction. Toward the end of the 2-hour period a little dilute H_2SO_4(1:3) was added to insure a complete reaction.

The apparatus was disconnected and 5 cubic centimeters of KI and 5 cubic centimeters of N/10 iodine solution were added to the receiving bottle. It sometimes was necessary to use a rubber policeman to break up the precipitate. To obtain accurate results the iodine should be in excess, as the KI dissolves the precipitate formed when AsH_3 is passed into a $HgCl_2$ solution and probably forms a double salt, K_2HgI_4. The iodine also oxidizes AsH_3 to As_2O_5, according to the familiar equations:

$$2AsH_3+6I_2+3H_2O=As_2O_3+12HI.$$
$$As_2O_3+2I_2+2H_2O=As_2O_5+4HI.$$

By titrating the excess of iodine with N/100 $Na_2S_2O_3$, using starch as an indicator, the quantity of arsenic was calculated indirectly from the iodine absorbed (8 parts of iodine to 1 of arsenic). Quantities of arsenic as small as 0.00005 gram were determined easily by this method. The accuracy of the method was tested with Na_3AsO_4 in a solution by itself and also when mixed with arsenic-free barberry tissue and alfalfa tissue. The results agreed with the calculations.

EXPERIMENTAL RESULTS

KILLING CONCENTRATIONS OF ARSENICAL SOLUTIONS

Several different commercial brands of sodium-arsenite solutions especially prepared for use in killing weeds and trees are on the

market. These vary considerably in strength and composition, some containing the equivalent of only 1 or 2 pounds of white arsenic per gallon, while others contain as much as 8 pounds per gallon. The relative quantity and the form of the alkali used vary also. Some brands contain a carbonate and others the hydroxide of sodium. Inasmuch as the transportation is the biggest cost item, it is apparent that the cheapest solution is that with the highest concentration of sodium arsenite. Most of the experiments reported in this bulletin were made with a sodium-arsenite solution which contained approximately the equivalent of 8 pounds of white arsenic per gallon. This solution is referred to as 8-pound sodium arsenite.

This 8-pound sodium arsenite, according to one manufacturer, is made from 8 pounds of white arsenic (As_2O_3) and about 2 pounds of sodium hydroxide (NaOH), with sufficient water to make a gallon. Each gallon weighs approximately 16 pounds. An analysis of a sample of this material by the United States Bureau of Chemistry gave the following results (per cent): Arsenious oxide As_2O_3, 49.98; sodium oxide, Na_2O, 10.01. Hypothetical combinations (per cent): Sodium metarsenite, $NaAsO_2$, 18.29; sodium acid arsenite, $NaH(AsO_2)_2$, 43.34; water, 38.37; total, 100.

As the relative amounts of alkali and white arsenic used in the manufacture of different brands of sodium arsenite varied considerably and as a number of railroad companies that use sodium arsenite to kill the weeds along the rights of way have secured better results with a solution containing more alkali than is used in the 8-pound material, pot experiments were performed to determine the most effective form to use. Theoretically a number of different forms of sodium arsenite are possible. They vary in the ratio of sodium to arsenic from the orthosodium arsenite, Na_3AsO_3, to the sodium-acid arsenite, $NaH(AsO_2)_2$. All of these may dissociate in solution to form more or less sodium hydroxide, NaOH, and arsenious acid, H_3AsO_3.

In Table 1 the toxicity of arsenious acid, sodium arsenate, and two sodium arsenites are compared. Small barberry plants in 3-inch pots were treated with sufficient quantities of the chemicals to obtain the indicated concentration of arsenic in the soil moisture.

TABLE 1.—*Effect of arsenic applied to small barberry plants in 3-inch pots*

Concentration of arsenic	Arsenious acid, H_3AsO_3	Sodium arsenite, Na_2HAsO_3	Na_3AsO_3+NaOH	Sodium arsenate
50 to 200 parts per million.	No injury	No injury	No injury	No injury.
400 parts per million	Slight injury to leaves	do	do	Do.
800 parts per million	Killed	Perceptible injury	do	Do.
1,600 parts per million	do	Killed	Perceptible injury	Slight injury.
3,200 parts per million	do	do	Killed	Killed.

This series was repeated several times with similar results. The concentration necessary to cause the death of the plants varied slightly, apparently owing to soil and atmospheric conditions, but the relative effectiveness of the different chemicals remained about the same.

Arsenious acid and the sodium arsenites were further compared in water cultures, using seedling barberries. The results of one of these series are shown in Table 2.

TABLE 2.—*Effect of arsenic applied to small barberry seedlings in water cultures*

Concentration of arsenic	Arsenious acid, H_3AsO_3	Na_2HAsO_3	Na_3AsO_3 +NaOH
25 parts per million	Injured	Healthy	Healthy.
50 parts per million	Dead	Injured	Do.
100 parts per million	do	Dead	Injured.
200 parts per million	do	do	Dead.

Here, again, it is evident that arsenious acid is more toxic than sodium arsenite and that the addition of more sodium to the solution reduces the toxicity. The solutions were prepared by first dissolving a given quantity of CP white arsenic in water to form the arsenious acid. Sufficient sodium-hydroxide solution was then added to portions of this arsenious acid to give the theoretical formulæ stated, after which the solutions were boiled. In this way it was certain that exactly equal quantities of arsenic were present in each of the three series.

It is interesting to note that much more dilute solutions caused the death of the plants in water cultures than in soil. This may be the result either of a physical absorption of the chemicals by the soil particles or of the formation of insoluble arsenic compounds caused by the presence of iron or other substances. It is conceivable also that, when iron or other chemicals which would have a tendency to form insoluble arsenic compounds are present in quantity, more alkali in the solution might reduce this action somewhat and allow the poison to act in the plant and in this way justify the use of solutions stronger in alkali than the 8-pound material chosen.

In another experiment seeds of various farm crops were sown in a dark silt-loam soil which contained 0.04 per cent of arsenic. This soil was obtained on November 17, 1923, from around the base of a large barberry bush that was treated on September 20, 1922, with sodium-arsenite solution. Undoubtedly the 0.04 per cent of arsenic remaining in this soil at the time it was collected was not all in the form of sodium arsenite, but no attempt was made to determine its chemical form. All the seeds used—oats, wheat, rye, barley, corn, pea, winter vetch, rape, and buckwheat—germinated well, and the plants grew to a height of 2 to 3 inches without noticeable injury. About that time some of the cereals assumed an unnaturally deep blue color and cases of tipburn developed. There also was a noticeable slackening in the rate of growth in all the plants in the arsenic soil, while the controls in arsenic-free soil continued to develop normally. Some of the plants were then dug and the root development compared. In the soil containing arsenic very few roots had developed, particularly in the oats, where the roots were only a few millimeters long (Pl. I, fig. 2). With pea, vetch, and corn the roots had grown about 1 centimeter but were brown and dying, and many short lateral roots had started (Pl. I, fig. 1, and Pl. II). The barley, wheat, and rye appeared to have been injured least by the

arsenic; but, except in the case of the rye, there was a very noticeable reduction in the length and vigor of the roots as well as in the tops (Pl. III). The rye continued to grow for more than a month and apparently had adapted itself to conditions when the experiment was discontinued.

The order of susceptibility of these plants was about as follows: Oat, pea, vetch, corn, barley, wheat, and rye. These observations agree with the results given by Voelcker (*45*) and show that although 0.04 per cent of arsenic in the soil did not prevent the germination of seed, it affected and prevented the growth of all the seedlings except rye.

ABSORPTION OF ARSENIC BY PLANT TISSUES

ABSORPTION THROUGH THE ROOTS

A review of the literature indicated that arsenic may be absorbed by many kinds of plants. To what extent common barberry plants would absorb sodium arsenite applied to the soil was of interest, not only as an indication of the manner in which the chemical kills the plant but because cattle occasionally browse on these bushes and might become poisoned. Analyses therefore were made of a number of treated plants. Table 3 contains the results. These barberry bushes were treated with the 8-pound sodium-arsenite solution according to the directions given by Thompson (*44*).

TABLE 3.—*Quantity of arsenic found in various portions of barberry bushes killed with sodium-arsenite solution applied to the ground*

Location	Date (1922) of—		Percentage of arsenic found in portion of plant analyzed						
	Treatment	Collection	Roots		Stems		Leaves	Fruit	
			Proximal	Distal	Proximal	Distal		Pulp	Seed
Toledo, Ohio	Aug. 17	Sept. 26	0.084	0.019	0.012	0.019	0.087	0.004	0
Marshall, Wis	Sept. 20	Sept. 30	.188	.019	.094	.024	.014	.009	0
Richland Center, Wis	Oct. 15	Nov. 2	.010	0	.007	.016	.075	0	0
Marshall, Wis	(Untreated)	Sept. 30	0	0	0	0	0	0	0

The variation in the quantities of arsenic absorbed by the plants at Toledo, Richland Center, and Marshall may be accounted for by a number of factors, among which are the date of treatment, variations in the quantity of sodium-arsenite solution applied, the texture and chemical properties of the soil, and the soil moisture. It was noted that the treatments at Richland Center were not so uniformly successful in killing the barberries as those at Marshall and Toledo.

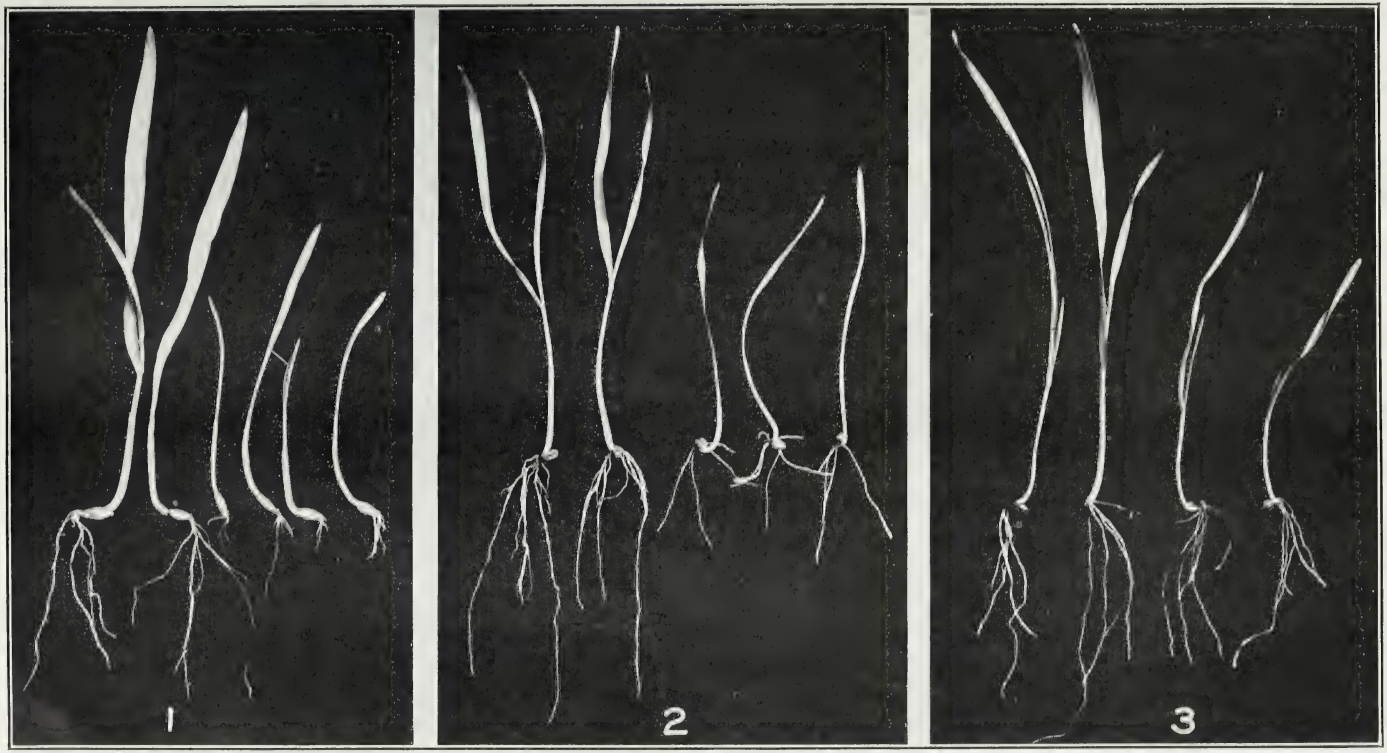
To establish the range of toxicity of arsenic and to determine its intake by plants, several groups of different plants, varying from grasses to trees, were treated and subsequently analyzed for arsenic. The plants were treated with solutions of the same concentration that was used on the barberry, but the quantities were varied in

EFFECT OF ARSENIC ON THE GROWTH OF SEEDLINGS.—I

FIG. 1.—Pea seedlings grown in arsenic-free soil (two on the left) and in soil containing 0.04 per cent of arsenic (four on the right). FIG. 2.—Oat seedlings grown in arsenic-free soil (three on the left) and in soil containing 0.04 per cent of arsenic (three on the right)

EFFECT OF ARSENIC ON THE GROWTH OF SEEDLINGS.—II

FIG. 1.—Vetch seedlings grown in arsenic-free soil (three on the left) and in soil containing 0.04 per cent of arsenic (three on the right). FIG. 2.—Corn seedlings grown in arsenic-free soil (two on the left) and in soil containing 0.04 per cent of arsenic (four on the right)



EFFECT OF ARSENIC ON THE GROWTH OF SEEDLINGS.—III

FIG. 1.—Barley seedlings grown in arsenic-free soil (two on the left) and in soil containing 0.04 per cent of arsenic (four on the right). FIG. 2.—Wheat seedlings grown in arsenic-free soil (two on the left) and in soil containing 0.04 per cent of arsenic (three on the right). FIG. 3.—Rye seedlings grown in arsenic-free soil (two on the left) and in soil containing 0.04 per cent of arsenic (two on the right)

FIG. 1.—COMPARISON OF THE ACTION OF SODIUM-ARSENITE SOLUTION APPLIED TO THE ROOTS AND TOPS OF TOMATO PLANTS

The tips of the roots of the plant in the left-hand pot were dipped 1 inch for three minutes in an 8-pound sodium-arsenite solution diluted 1 to 40. The tip of the stem of the plant in the center pot was dipped for the same length of time, and one leaf of the plant in the right-hand pot was dipped

FIG. 2.—SMALL BARBERRY TREATED WITH SODIUM-ARSENITE SOLUTION

The base of the stems was wet with the solution, and in drying some arsenic remained on the surface. Lambs gnawed the bark and secured sufficient arsenic to cause the death of several

proportion to the size of the plant. They were treated in the field in their natural habitats, and the quantity used was in no case more than 2 gallons per plant. Table 4 gives the results.

TABLE 4.—*Quantities of arsenic found in plants treated with sodium arsenite*

Name of plant		Date treated	Date sampled	Arsenic (per cent) found in—		
Common	Latin			Leaves	Inflorescence	Entire plant
Alfalfa	Medicago sativa L.	Aug. 25	Aug. 28	0.231		
Barberry	Berberis vulgaris L.	do	do	.95		
Barnyard grass	Echinochloa crusgalli L.	do	Sept. 4			0.014
Beet, sugar	Beta vulgaris L.	do	Aug. 28	.018		
Boxelder (4 feet high)	Acer negundo L.	do	Sept. 4	.047		
Chicory	Cichorium intybus L.	do	do			.026
Clover, sweet	Melilotus alba Desr.	do	do			.040
Cocklebur	Xanthium echinatum Murr.	do	Aug. 28	.056		
Corn	Zea mays L.	do	do	.040		
Lettuce, wild	Lactuca canadensis L.	do	Sept. 6			.049
Morning-glory	Ipomoea coccinea L.	do	Aug. 28			.056
Pine	Pinus strobus L.	do	do	.018		
Plantain	Plantago major L.	do	do			.040
Plum, wild (5 feet high)	Prunus americana Marsh.	do	do	.021		
Poplar (10 feet high)	Populus deltoides Marsh.	do	do	.14		
Quackgrass	Agropyron repens L.	do	Sept. 4			.030
Russianthistle	Salsola kali tenuifolia G. F. W. Mey.	do	do			.026
Sorrel	Rumex hastatulus Baldw.	Sept. 8	Sept. 11			.057
Sunflower	Helianthus annuus L.	Aug. 25	Aug. 28	.148	0.143	
Sumac (3 feet high)	Rhus glabra L.	do	Sept. 6	.018		
Turnip	Brassica rapa L.	Sept. 8	Sept. 11	.018		
Virginia creeper	Parthenocissus quinquefolia Planch.	do	do	.010		
Willow	Salix cordata Muhl.	Aug. 25	Aug. 28	.17		

Symptoms of poisoning occurred in all cases on the third or fourth day, and all treated plants died. The leaves were soon altered in appearance, the green color becoming whitish or brownish, starting from the margins and developing inward. The more succulent plants withered and collapsed, and the poplar leaves turned black. The poplar was particularly sensitive to the poison. It was a small tree about 10 feet high and grew in waste land in sand. Other poplars 10 feet away from the treated tree died also. Evidently the arsenic came into contact with the roots. This fact demonstrates the rapidity with which the poison acts. Wild cherry and oak appeared less susceptible than the other plants.

Alfalfa, barberries, and turnips growing in the same general location as those given in Table 4 but which were not treated with sodium arsenite were analyzed, and no arsenic was found.

ABSORPTION THROUGH TOPS OR LEAVES

Repeated attempts with sprays applied to the leaves and tops of the bushes have failed to kill common barberries. Sodium-arsenite solution and several other chemicals were tried, but in all cases except seedling barberries numerous sprouts developed from the roots of the sprayed bushes even though the tops were killed. As most recommendations for the use of chemicals as weed killers have been to spray the plants and as spraying has been successful even with perennial plants that propagate by stolons, a few experiments were

performed to determine the extent to which arsenic applied to the tops of plants is carried to the roots.

In the case of the barberry near Toledo, Ohio, reported in Table 3, the distal roots were collected at a point about 4 feet distant from the crown and more than 2 feet beyond the point of application of the sodium-arsenite solution. The ground was level and sandy, and there was no indication from killed grass or otherwise that the solution had spread in the soil to that distance; yet arsenic was found in the roots, indicating that it might have been absorbed near the crown of the bush and transported within the roots toward their distal ends.

Swingle and Morris (*43*) report that arsenic solutions applied to wounds in the limbs of apple trees were carried both up and down the limb. They state that "as a rule, it [the injury] extends farther upward than downward; but the reverse is sometimes true." The dead areas resulting from the entrance of the arsenicals in their tests frequently extended from 2 to 5 feet above the point of entrance and occasionally to a distance of 3 feet below.

Many other workers have reported similar phenomena. In general, the transportation toward the top of the plant has been found greater and more rapid than in the reverse direction, and Bose (*8*) has concluded that the ascent of sap is eight times as rapid as the descent.

A few experiments were performed by the writers in order to compare the action of sodium-arsenite solution applied to the roots and to the tops of plants. The plants used were small barberries, tomatoes, peppers, geraniums, cucumbers, and potatoes. Plate IV, Figure 1, illustrates the results with one series of tomatoes. In the first pot only 1 inch of the ends of the roots was dipped in 8-pound sodium-arsenite solution diluted 1 to 40. In the second pot the tip of the plant was dipped in the same solution for a period of three minutes, and in the third pot one leaf was dipped for the same length of time.

In every case where a portion of the root was dipped, the entire plant began to wither within a few hours and eventually died, whereas in only a few cases did the injury from top dipping extend beyond the portions actually dipped. It also was observed that when the tops were dipped plants with suberized leaves, such as the barberry, were injured less than plants with softer leaves.

RATE OF LEACHING OF SODIUM ARSENITE FROM SOILS

A fair-sized barberry bush growing in a wood lot in well-drained soil rich in leaf mold was treated with 2 gallons of a 1 to 40 dilution of 8-pound sodium arsenite on September 20, 1922. Samples of the surface soil from around this bush were collected on different dates and the quantities of arsenic present determined. The results are given in Table 5. The slight increase in the quantity of arsenic indicated on two different dates probably is due to irregularities in the distribution of the chemical and in the sampling.

TABLE 5.—*Rate of leaching of sodium arsenite from soil*

Date sampled	Arsenic found	Total precipitation after treatment	Date sampled	Arsenic found	Total precipitation after treatment
	Per cent	*Inches*		*Per cent*	*Inches*
Sept. 28, 1922	0.676	0	June 25, 1923	0.132	18.32
Oct. 8, 1922	.423	.06	Oct. 10, 1923	.100	31.10
Oct. 18, 1922	.222	.56	Nov. 17, 1923	.040	33.40
Apr. 10, 1923	.258	12.76	Apr. 12, 1924	.056	40.84

It is apparent that the leaching of the arsenic from this surface soil was very rapid and extensive and that the greater part disappeared within a year of the application. Undoubtedly in more arid climates the leaching would have been less rapid, and in more humid climates it might have been still more rapid. However, McGeorge (*35*), working in Hawaii with an annual rainfall of about 200 inches, found practically no leaching of small quantities of arsenic from the surface soil, even over a period of several years. The mineral constituents in the soil may play an important part in this, or it may be that a limited quantity of arsenic may be held indefinitely and only the excess leached out.

At the time of the sampling on November 17, 1923, some of the soil was brought to the greenhouse and seeds of a few varieties of the common economic plants sown in it to determine whether arsenic would be taken up. The results are shown on pages 9 and 10 and in Plates I, II, and III.

SODIUM ARSENITE AND FARM ANIMALS

Incidental to the use of sodium arsenite in eradicating the common barberry, a number of fatalities among farm animals have occurred. Although very few compared with the number of treatments made, they are worthy of record as indicating the dangers in the use of this material and the precautions necessary to avoid loss.

Analyses of barberry tissues showed such small quantities of arsenic that little apprehension was felt from this source, but it was recognized that sodium-arsenite solution spilled on the grass might be dangerous. That this fear was justified was shown in one instance when a few bushes in a pasture were treated. Cattle had access to the pasture and they found a place about 2 feet in diameter where some of the solution had been spilled. A few ate not only the grass but quantities of the sand also, with fatal results. Analyses of the stomach contents showed the presence of arsenic.

In another case in a different State two cows were killed by eating sand from around the base of a barberry plant to which sodium arsenite had been applied. In this case a shallow trench had been dug around the base of the bush and the poison poured in it. The weather was hot and dry, and no rain had occurred during the week to wash the arsenic into the soil. As the farmer had agreed to keep his cattle out of the pasture for a week, the men neglected to fill the trench, with the fatal results noted.

Another case of a slightly different nature occurred on another farm. Several small barberry plants were treated with the sodium-

arsenite solution. The solution was poured into the center of the crown and around the bottom of each bush, but not on the leaves or top, and none was spilled on the ground other than at the base. Stones, sticks, and sod were then piled around the bushes, effectively covering the treated ground. A number of young lambs were turned into this pasture a few days after the treatment and found one of the treated bushes. They gnawed the bark from the base of some of the shoots (Pl. IV, fig. 2), and several obtained sufficient arsenic to cause death. These shoots had been wet by the solution, and in drying sufficient arsenic had remained on the surface to produce the fatal results. In this case, as in the previous one, no rain occurred between the time of treatment and the time the lambs gnawed the bushes.

DISCUSSION

A review of the literature on arsenic, primarily sodium arsenite, in its relation to uses for weed killing, reveals the fact that arsenic has been extensively used for this purpose with good success and with no apparent permanent damage to the soil, which of necessity becomes the recipient of the substance. Soil organisms, such as bacteria, have been stimulated by small quantities of arsenic, and even higher plants grown on arsenic soils have shown stimulation, as manifested in increased growth.

Incident to the use of arsenic, its extreme toxicity to animals had to be considered, and the literature cites numerous cases of poisoning cattle, sheep, and horses from arsenic obtained from different sources, such as some smelter emanations and solutions used in weed eradication. It has been discovered that cattle are attracted by the taste of arsenic. Repellents, such as aloes, have been used with success. These would eliminate the most undesirable feature in the use of arsenic.

The experimental results presented in this bulletin give further information on some effects of arsenic when used for killing the common barberry. In preliminary greenhouse experiments it was found that the arsenious acid was the most toxic to the barberry. The sodium arsenites were less toxic, and of these the trisodium was the least toxic.

Field practice has shown that 2 gallons of a solution prepared from 1 gallon of commercial sodium arsenite containing the equivalent of 8 pounds of white arsenic and diluted with 40 parts of water were sufficient to cause the death of a single bush of the common barberry. Killing was effected within three to seven days. Chemical analysis showed that the killed plants had absorbed arsenic in nearly all parts, and the quantities in vegetative tissues varied from 0.007 to 0.188 per cent. Numerous other plants, including grasses and trees, were tested, and all were killed by the solution specified, arsenic being found in their tissues. The poplar appeared very sensitive to arsenic poisoning and the wild cherry and oak the least susceptible.

Spraying the aboveground portions of various plants with a solution of arsenite identical with the one used for application on the roots showed that only the treated portions were killed, and then only in the case of tender plants. Plants with waxy or leathery leaves were not affected when held in the solution for three minutes.

This suggests that spraying may fail to kill some plants and also that spraying the aboveground portions of plants may not result in arsenic being carried to the roots or tubers, thus leaving these portions safe for animal or human consumption.

The soil treated with sodium arsenite incident to killing the barberry showed moderately fast leaching. The arsenic content decreased from 0.676 per cent at the time of application to 0.040 per cent after 14 months in well-drained soil under an annual rainfall of about 30 inches.

Various economic plants seeded in this soil containing 0.04 per cent of arsenic showed no inhibition of germination, but growth was affected. Plants belonging to different families showed varying susceptibility. Legumes proved to be the most susceptible and rye the most resistant.

Although precautions were taken to prevent animals from having access to the arsenic, accidents occurred in different States where barberries were treated. The animals sought arsenic and consumed parts of plants and soil to which arsenic had been directly applied. This experience demonstrates the necessity of finding a repellent that will alter the taste, if it is desired to continue the use of arsenic as a weed killer.

A modified method for determining small quantities of arsenic in plant tissue was found useful in these experiments.

SUMMARY

A modified volumetric method for the determination of small quantities of arsenic in plant tissue was developed and proved to be rapid and accurate.

Sodium arsenite in proper dilution was an effective killing solution for most plants. The arsenious acid was the most effective form of arsenic tested.

Arsenic was found in nearly all tissues of treated plants, while the controls contained no arsenic.

Arsenic was most effective in killing plants when applied to the roots. Spraying or dipping was not always effective.

The soils used showed rapid leaching of sodium arsenite where rainfall was abundant.

The characteristic brackish sweet taste of arsenic attracted animals, and it was found that the use of sodium-arsenite solution in pastures without precautions or repellents was not safe.

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